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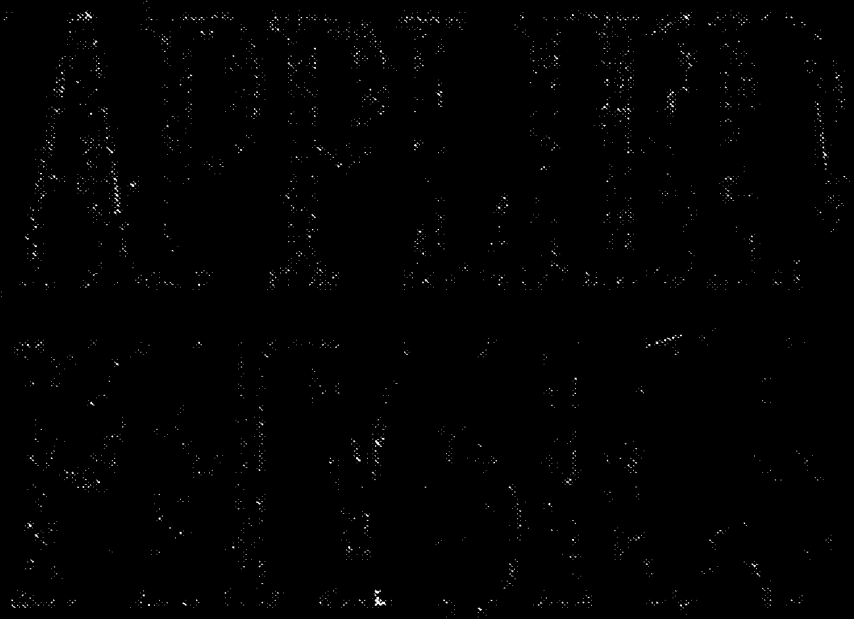

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Growth of suspended carbon nanotube networks on 100-nm-scale silicon pillars

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We investigated carbon nanotube growth by means of methane chemical vapor deposition on ultrafine silicon patterns prepared by synchrotron-radiation lithography. Grown nanotubes formed suspended bridges between pillars when pillar spacing was comparable to pillar height. Network-like interconnections were obtained on pillar arrays. Nearest-neighbor bridging accounted for more than 80% of all the bridging nanotubes. The self-directed growth between neighboring pillars may be explained by the swing of the nanotube cantilever which contacts a catalyst particle in liquid phase as the nanotube grows. These results confirm the possibility of self-assembled wiring of nanostructures. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1507840]

Carbon nanotubes are self-assembled nanoscale structures with excellent mechanical, electrical, and chemical properties useful for a variety of applications.[1] In nanoelectronics, semiconducting carbon nanotubes act as a field effect transistor[2] or a single electron transistor.[3] Metallic carbon nanotubes exhibit ballistic conductivity at room temperature.[4] The ballistic conductivity and mechanical strength of carbon nanotubes, as well as their shape and size, make them ideal for the wiring of nanoscale devices. We have proposed self-assembled interconnection of nanostructures by carbon nanotubes.[5] This would provide a means of configuring logics consisting of self-assembled nanostructures. Self-directed growth of suspended nanotube networks was first demonstrated by Cassell *et al.*[6,7] They used arrays of 10 μm high silicon towers and grew nanotube networks by printing liquid-phase catalyst precursor selectively on the tower tops by means of chemical vapor deposition (CVD). This self-directed growth is a remarkable feature of carbon nanotubes. However, the growth mechanism is not understood yet. Controllability of the growth site, yield, diameter, and chirality are other issues that should be investigated. Zhang *et al.* recently showed that an electric field has a prominent effect on the alignment of single-walled carbon nanotubes on a patterned substrate.[8] This is an effective way to control the direction of growth. We are still concerned with the self-assembling nature of suspended nanotube growth. In this letter, we report the synthesis of carbon nanotube networks on an array of 100 nm diameter silicon pillars. The directional growth mechanism is discussed based on observation of 2000 pillars.

A patterned Si (001) substrate was prepared using synchrotron-radiation lithography. The patterns consisted of a two-dimensional lattice of silicon pillars (diameter: 100 nm, height: 360 nm, pitch: 500 nm). Specimens were chemically oxidized in H_2O_2/H_2SO_4 (1:4) solution, and then deposited with a catalyst thin film using a conventional vacuum evaporator. The thickness of the deposited film was 1 nm or less. The furnace for CVD experiments consisted of a quartz tube with a carbon heater mounted inside a stainless steel chamber. The specimen (10×10 mm^2 or smaller) was placed on a carbon plate (80 mm diam) above the heater. CVD was performed with methane gas flowed at 300 cm^3/min at the gas pressure of 500 Torr and 950 °C for the Fe catalyst, and at 200 Torr and 800 °C for the Co catalyst. After growth, the specimens were observed with a high-resolution scanning electron microscope (SEM) (Hitachi S-5000). To make the SEM observation easier, Pt was deposited onto the specimen to decorate the suspended nanotubes.

We have already reported that single-walled nanotubes (SWNTs) were selectively obtained on a Si substrate when methane was used in combination with Fe_2O_3 nanoparticles at the growth temperature of around 950 °C.[9] The advantage of Fe_2O_3 nanoparticles over Fe nanoparticles is that particle diameter stays small during CVD owing to the nonagglomerating feature of Fe_2O_3 nanoparticles. A similar result was obtained when an Fe thin film of 1 nm or less was deposited on Si. This might be due to oxidation of the thin Fe film. SWNTs were also obtained by using methane CVD with a Co catalyst at 800 °C. For Co, the particle size did not affect the SWNT growth. At a higher temperature, however, silicidation of Co inhibited nanotube growth.

Nanotubes grown on Si mesa structures frequently showed suspended growth between mesas. Figure 1 shows nanotubes grown on 100 nm diameter Si pillars when the catalyst was Fe. Most nanotubes started growing from pillar tops and connected between pillars, forming a network. Some nanotubes extended from one pillar to another, and others just connected two neighboring pillars. Most connected nearest-neighbor pillars, but the connection between second-nearest neighbors were also seen. There were many nanotubes formed on the substrate surface. They extended

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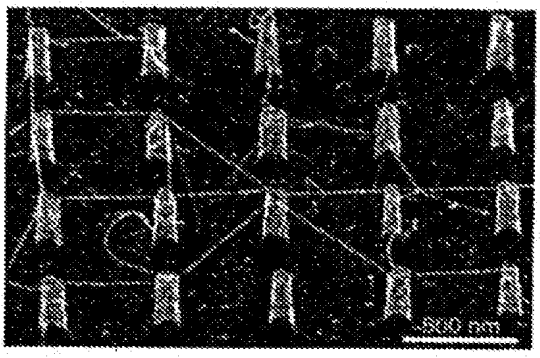

FIG. 1. SEM images of carbon nanotubes grown on Si pillars using Fe thin film catalyst at 950 °C. Pt was deposited to highlight nanotubes. For SEM imaging, a 30 keV electron beam was used at the incident angle of 40°.

along the surface, and were thus hard to observe after Pt coating.

Similar suspended growth was also seen for the Co catalyst (Fig. 2). Connections between the nearest-neighbor pillars were seen. For Co, the connectable range was less than 1 μm, so most of the nanotubes connected nearest-neighbor pillars. The short range may be due to the lower growth temperature, 800 °C.

The nanotube growth behavior in Figs. 1 and 2 is basically the same as that seen when 50 times larger structures and a different type of catalyst were used,[6,7] except for the smaller connectable range of the Co catalyst case. We think that most of the nanotubes are individual SWNTs, because we used the selective SWNT growth condition previously examined on a flat Si substrate,[9] and the yield is not high enough to grow bundles of SWNTs. Double-walled nanotubes could also possibly exist. We have observed by transmission electron microscopy double-walled nanotubes grown on a flat Si substrate.

There were various types of suspended nanotubes in the pillar array. Typical images are presented in Fig. 3. Panel (a) shows nearest-neighbor connections. The image shows a mutual connection among four neighboring pillars, but most of the connections are just between two neighboring pillars. Although the nanotubes in (a) are straight, an arch shape was often observed [see panel (e)]. Panel (b) is a second-nearest-neighbor connection. Longer connections, as in panel (c), could be found, but less frequently. Panel (d) shows a complex connection with a double y-junction shape. This is most likely formed by tangling of two adjoining arches connecting

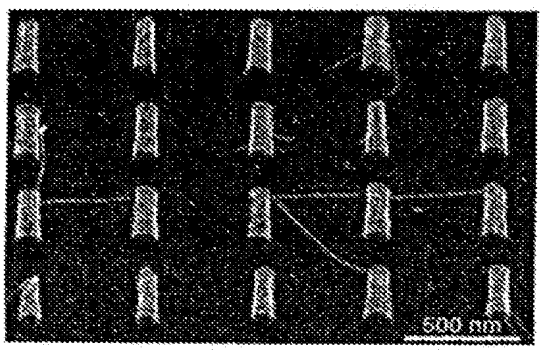

FIG. 2. SEM image of carbon nanotubes grown on Si pillars using Co thin film catalyst at 800 °C. The observation conditions are the same as in Fig. 1.

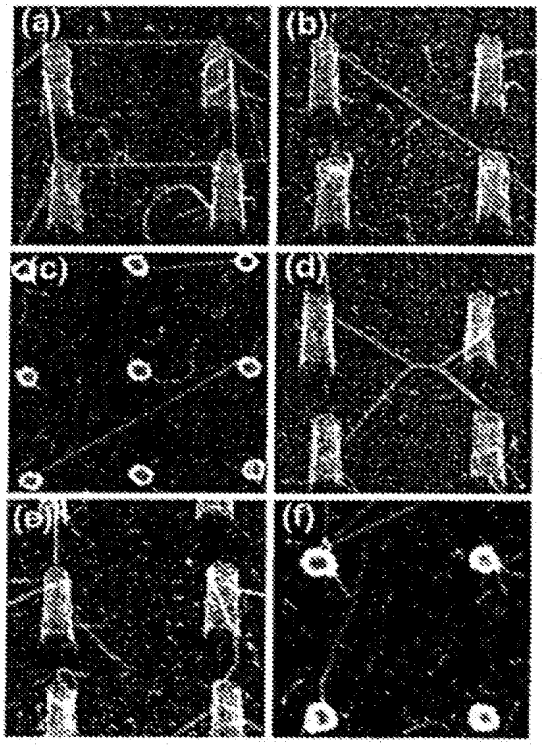

FIG. 3. Various types of nanotubes grown on Si pillars using Fe thin film catalyst at 950 °C. The pillar spacing is 400 nm. (a) Nearest-neighbor connections; (b) a second-nearest-neighbor connection; (c) a longer-distance connection (top view); (d) double "y junctions;" (e) a fallen nanotube; and (f) an open-ended nanotube (top view).

nearest neighbors, as discussed later. In other cases, nanotubes fell to the substrate (e) or terminated before reaching another pillar (f).

The growth of the different types of nanotubes on the pillars was investigated statistically through SEM observations of about 2000 pillars for both Fe and Co catalysts. The results are summarized in Table I for each catalyst. For the Fe catalyst, nanotube growth in any style was seen among 76% of the pillars examined. Among them, the fraction of bridging nanotubes was 45%, that of fallen tubes was 40%, and that of tubes halfway terminated was 15%. Surprisingly, 86% of the bridging tubes connected nearest neighbor pillars. The second-nearest-neighbor connection was only 9%. Therefore, 29% of nanotubes originating from the pillar top achieved the interconnection between nearest-neighbor pillars. Similar statistics were found for the Co catalyst. The yield of nanotubes was lower for the Co case: nanotubes

TABLE I. Fractions of nanotube types grown on Si pillars.

	Fe catalyst	Co catalyst
Total number of pillars	2004	1980
Pillars with nanotubes	76%	43%
Fallen nanotubes	40%	39%
Open-ended nanotubes	15%	18%
Bridging nanotubes	45%	43%
Nearest-neighbor bridges	86%	83%
Second-nearest-neighbor bridges	9%	13%
Others	5%	4%

were seen among 43% of 1980 pillars. The fractions of bridging, fallen, and halfway-terminated tubes were 43%, 39%, and 18%, respectively. Among bridging nanotubes, 83% showed a nearest-neighbor connection, and 13% showed a second-nearest-neighbor connection. The ratio was essentially the same as in the Fe catalyst case.

Such a relatively large fraction of the nearest-neighbor interconnection can be obtained when the aspect ratio of pillar is large and the pillar spacing is comparable to the pillar height. When the pattern spacing was much larger than the pattern height, nanotubes often failed to connect patterns directly and they fell to the substrate. Therefore, the suspended growth is due to a geometrical effect. The methane flow, which was supposed to keep the nanotubes floating,[7] is unlikely the cause of suspended growth because of the lower pressure and smaller methane flow rate in the present case. Here is a rough estimation of the lift provided by the methane flow. From the mass conservation, $\rho v S = \text{constant}$, where ρ is the density of the methane gas, v is the flow velocity, and S is the cross section of the gas line. The ρ is proportional to the pressure, P, and the initial gas flow vS is $300\ \text{cm}^3/\text{min} = 5\ \text{cm}^3/\text{s}$. The cross section of the quartz tube at the specimen was $0.25 \times 3.2\ \text{cm}^2$. Thus, the methane flow velocities at 500 and 200 Torr are 6 and 15 cm/s, respectively. Suppose a SWNT with a diameter d is located perpendicular to the gas flow. The lift due to an ideal gas flow with velocity v would be of the order of $\rho v^2 d$ per unit length. For a 400 nm long SWNT with $d = 2$ nm, the force amounts to only 10^{-18} N, which is greater than the gravity ($\approx 10^{-20}$ N) but much smaller than the aligning force due to the electric field estimated by Zhang *et al.* ($\approx 10^{-6}$ N).[8]

Nanotubes originating from pillar tops can extend in any direction. However, if a nanotube starts to grow on the plane of the pillar top, the tube is likely to grow along the pillar top surface and thus extend parallel to the substrate surface. As a nanotube extends, it forms a cantilever with a large aspect ratio, so the open end of the nanotube should vibrate during extension. If the vibration amplitude is large, the nanotube would contact a neighboring pillar. The thermal vibration amplitude of a SWNT at 900 °C was estimated to be as large as 6 μm when the tube length L was 20 μm.[8] But, the amplitude is proportional to $L^{3/2}$,[10] and it is estimated to be only 18 nm for a 400 nm long SWNT. An example of the vibration of a cantilever nanotube can be seen in Fig. 3(f). This was a Pt-coated SWNT, but its vibration amplitude was almost the same as that of an uncoated SWNT. The amplitude is about 15 nm (a full width of 30 nm), which is in good agreement with the calculated thermal amplitude of 12 nm for a 500 nm long SWNT at room temperature. These values are quite modest, and cannot explain the large fraction of nearest-neighbor bridging. The vibration frequency of a SWNT calculated using the equation in Ref. 10 is of the order of 10^2 MHz, which is hardly enhanced by the mechanical vibration of the CVD apparatus.

We think that the catalyst particles melt in the growth ambient, because we observed that nanotubes on the substrate penetrated many catalyst particles.[9] Therefore, when a nanotube contacts the pillar only at a catalyst particle, the nanotube may swing or even revolve around the catalyst particle due to the mechanical vibration of CVD apparatus. Thus, the probability of making contact with a neighboring pillar should be high. The nearest-neighbor-bridging fraction of $>80\%$ can only be explained by a swing amplitude as large as the pillar spacing. Once a nanotube contacts a neighboring pillar, the growth orientation is fixed and the tube extends from one pillar after another.

Nanotubes can grow upward or downward from the pillar top. Downward growing nanotubes just fall to the substrate. Upward growing ones often form an arch between pillars. If the arch is long enough, the central part of the arch can touch the substrate surface due to vibration or revolution. This causes a nanotube to fall from both ends at the pillar tops, and explains the absence of tall arches. If two adjoining arches are formed, they can touch each other, resulting in the shape shown in Fig. 3(d).

In conclusion, we have confirmed that suspended nanotube bridges were formed between neighboring pillars with a high probability even on a 100 nm scale, where the thermal vibration of a nanotube cantilever was small. The interconnectional growth of nanotubes between mesa structures is very promising for the self-assembly of interconnections. The probability of nearest-neighbor connection can be increased by reducing the spacing between mesa structures. Thus, even for quantum dots, nanotube interconnections could be formed when the dot spacing is small.

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